64-3

THERMO ELECTRON

ENGINEERING CORPORATION

ASD-

Report No. TE-11-64

Thermo Electron Engineering Corporation, 85 First Avenue, Waltham, Massachusetts, 02154

THIRD QUARTERLY REPORT
FOR
ADDITIVE CONVERTER STUDIES

By

S. S. Kitrilakis

September, 1963

Contract No. AF 33(657)-10130

Prepared for

Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio

Approved: S. Kitrilakis
S. S. Kitrilakis, Manager
Research Department

FOREWARD

The work covered by this report was accomplished under Air Force Contract No. AF 33(657)-10130, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

TABLE OF CONTENTS

Chapter		Page
I	INTRODUCTION	1
II	EXPERIMENTAL RESULTS	3
	1. Performance	3
	2. Collector Work Function	4
	3. Emitter Work Function	5
	4. Corrosion Tests	6
III	PLANS FOR NEXT QUARTER	9
	Reference	10

LIST OF ILLUSTRATIONS

Figure		Page
1	Family of Current-Voltage Curves Cs and CsF present at T_e = 1785° K	11
2	Comparison of Envelopes at T_e = 1785° K With and Without CsF	12
3	Power Output Comparison	13
4	Current-Voltage Curves Compared to Envelopes	14
5	Current-Voltage Curves Compared to Envelopes	15
6	Current-Voltage Curves Compared to Envelopes	16
7	Collector Work Function	17
8	Emitter Work Function	18
9	Re Emitter Surface at 1085 x from CsF Converter	19
10	Re Emitter Surface from Cs Converter	19

LIST OF ILLUSTRATIONS (Cont'd)

Figure		Page
11	Mo Collector Surface at 300 x	20
12	Mo Collector S pot at 1085 x	20
13	Inside Portion of Seal at 150 x	21
14	Outside Portion of Seal at 150 x	21
15	Tantalum Thin Wall Spacer	22
16	Tantalum Thin Wall Spacer	22

SUMMARY

During the third quarter of this program a Re emitter- Mo collector converter was tested with Cs and CsF additive. This same converter had been tested in the previous quarter with Cs only and its performance agreed well with the documented performance of similar devices. The most significant effect of the CsF observed is a lowering of the collector work function by 0. 1 to 0. 15 volts. This collector work function reduction is evident in retarding plot measurements and in the increase of the output voltages at the "knee" of current-voltage curves.

The effect of the additive on the work function of the emitter has not been clearly formulated at this time. Under conditions of high power output the emitter work function appears unaffected. At lower Cs pressures, however, an increase in work function is observed for high CsF arrival rates, while low CsF arrival rates result in work functions lower than the Cs-only case.

A Re emitter - Mo collector converter was operated for 150 hours with Cs and CsF additive and then subjected to metallurgical examination to reveal any corrosive effects of the CsF. The emitter, collector and seal structures were examined and no corrosion attributable to the presence of CsF was detected.

CHAPTER I

INTRODUCTION

During this quarter, the program moved into the second phase of experiments designed to study the effects of cesium halide vapors on the performance of thermionic converters. This phase consists of testing a Re emitter Mo collector converter with CsF in addition to Cs. The first phase was concerned with the vacuum and cesium characteristics of the converter. The object of that sequence of experimentation was to establish a reference performance deviation which could then be attributed to the presence of CsF. The reference performance documentation consisted of three ~~kinds~~ of data:

a. Current voltage curves in the region of high power generation were obtained to a sufficient extent to confirm that this device followed the performance maps generated in the past for the Re-Mo system.

b. Emitter work function values were obtained at various combinations of emitter and Cs reservoir temperatures.

c. Collector work functions were computed from retarding plots.

The purpose of documenting emitter and collector work function variation as well as performance was to make possible the correlation of performance changes with changes in these parameters.

The section on experimental results that follows presents experimental evidence of increased output power of the test converter in the range of emitter temperatures of 1600° to $2000^{\circ}K$ after the CsF was introduced. This increase comes about from an increase in output voltage and, therefore, is the most desirable form of increased performance since it implies a proportional increase in efficiency.

Measurements of emitter work function indicate a complex dependence of this variable on emitter temperature, Cs arrival rate, and CsF arrival rate. At this time a correlation of these variables has not been achieved. The collector work function measurements indicate that lower values are obtained when the CsF is present.

The results of corrosion tests are presented in the form of metallographs of the emitter and collector surfaces and the seal structure. Longer duration tests will follow, but is seems at this time that no serious corrosion problem exists.

CHAPTER II

EXPERIMENTAL RESULTS

1. Performance

The primary objective of this program is to document any changes in converter performance brought about by the presence of cesium halide vapors in the converter. The most direct approach to this objective is the systematic compilation of current voltage curves. The basic building block of such a parametric study is a family of current-voltage curves obtained by letting the cesium reservoir temperature vary while the remaining variables are held constant. Figure 1 is a family of curves obtained at an emitter temperature of 1780° K, a spacing of 0.022", and a collector temperature of 848° K. The cesium reservoir temperature was varied from 543° to 623° K. Each current-voltage curve in Figure 1 is tangent to an envelope indicated by the dashed line. This envelope is the locus of the maximum current obtainable at any given voltage by optimizing Cs pressure for a given emitter temperature and spacing. The existence of this envelope makes possible for more meaningful comparisons of performance than the use of single current-voltage curves would allow.

A 10° K change in the cesium reservoir temperature, for example, results in double the current value at low voltages for a given curve. Use of the envelope, however, eliminates the effect of this variable.

The above reasons dictated the use of such envelopes as the basis for comparisons in the present work. As a first step in the evaluation of the effects of CsF, families and individual current-voltage curves were taken over the 1600° - 2000° K range of emitter temperature and were compared to the envelopes obtained with Cs only. Figure 2 shows the envelopes for the families of curves with and without

CsF at 1785° K emitter temperature and spacings around 0.02". The envelope corresponding to the CsF family is higher than the Cs only envelope by a substantial amount, especially at higher output voltages. The change appears to be an increase in output voltage suggesting a lowering of collector work function. The range of cesium reservoir temperature required is at a higher level in the CsF case. This fact suggests that a higher Cs pressure is necessary in CsF cases to achieve the same emitter work function. These possibilities will be further examined when the emitter and collector work function measurements are discussed. Figure 3 is a comparison of the output powers associated with the envelopes in Figure 2. The gain in power output and especially in efficiency are significant since the same power is obtained at 25-30% higher voltages. Figures 4, 5 and 6 demonstrate the same effect of the CsF over the entire emitter temperature region. The spacing values tested are only 0.002" and 0.022" and consequently , spacing has not been optimized. Optimum spacing is related to Cs pressure and therefore a different optimum should be expected in the CsF case. When this optimum is obtained, a further gain in performance is quite probable.

In all instances of current-voltage tests, the CsF reservoir temperature was varied. In all cases, however, the characteristics were observed to be independent of the CsF reservoir temperature. The range of variation was limited to 600° to 1000° K and apparently within this range the collector is saturated with CsF. This conclusion is substantiated by Reference 1. In future experiments much lower CsF reservoir temperatures will be investigated.

2. Collector Work Function

The retarding potential method was used to determine collector work functions There is doubt as to the accuracy of the absolute value of the work function measurements obtained in the manner because the effect of ion current cannot be readily separated and edge effects may also influence the results. However, a great deal of data have been obtained in identical devices in this manner and collector work functions have been correlated with the ratio of collector temperature to Cs reservoir temperature. It was felt, therefore, that values of collector work functions obtained in this manner in the CsF case could be compared on a relative basis to the ones in the Cs-only case. Figure 7 shows the correlation of work functions of cesiated molybdenum collectors from several devices as well as the present device before CsF was introduced. The shaded area indicates the spread in work function values. Although the correlation is by no means complete, certain trends appear. The values obtained in the presence of CsF are 0.1 to 0.2 volts lower. The location of the minimum value appears to have shifted from a T_C/T_R value of 1.9 to 1.4 or 1.5. This is especially significant since this is the region of converter operation that results in high output powers. This result is in line with the improvement in performance observed in the current voltage data. Variation of the CsF reservoir temperature from 530° to 700° K did not result in any change of collector work function; the reason for this is suspected to be that the collector surface is saturated at some arrival rate corresponding to reservoir temperatures lower than 530° K. Further experimentation will investigate this lower arrival rate region.

3. <u>Emitter Work Function</u>

The dependence of the work function of cesiated Re on surface temperature and cesium reservoir temperature has been determined in the past by this group, (See Reference 2). The emitter work function of the present device was determined prior to the introduction of CsF and was reported in the last quarterly report. These measurements agreed with all previous work. These work function determinations are all obtained from saturation current values under ion-rich conditions.

At this time, two series of emitter work function runs have been conducted. In both cases, the variations in the CsF reservoir temperature resulted in no change, indicating that the surface was apparently saturated with CsF. The data are ploted in Figure 8 in the form of dark and light circles. The solid line is the correlation for Cs on Re. Both sets of data indicate a higher work function for a given surface temperature and cesium reservoir temperature. This is in agreement with the fact that the current voltage curves require somewhat higher cesium reservoir temperature in the CsF case. Both sets of data follow lines of lesser slope than the cesiated Re line. The amount of data available at this time do not allow any correlation of the variables. It is obvious, however, that measurements at low CsF arrival rates are necessary before the relationships can be understood.

4. Corrosion Tests

A typical converter operated for about 150 hours with Cs and CsF inside was opened and examined to ascertain the corrosive effects of CsF. Prior to the metallurgical examination, the converter was opened to air. Apparently some metallic Cs remained in the converter although an attempt was made to remove all Cs. The moisture in the air rapidly formed CsOH in aqueous solution which caused some secondary corrosion.

A metallograph of the Re emitter surface is shown in Figure 10. This emitter surface appeared quite typical of the Re run for some time in a converter. A network of grains varying greatly in size is seen, and individual grains are perceptibly not flat. The grain boundaries are very clearly delineated, and there may be some slight attack on impurities segregated at them, but if so, it is due to Cs and not to CsF, since the appearance of a Re emitter removed from another tube is very similar (Figure 10). In neither case is there apparent attack of the Re surface.

Most of the collector is covered with a thin layer of dark material which is probably an oxide of Mo. Similar deposits have been found in other converters in the past. The deposited layer is fairly uniform over the center of the collector, but at the edges different grains are often differently colored, suggesting a surface reaction proceeding at a rate depending on the orientation of the grain. No grain boundary attack or pitting is discernable.

Several spots are visible to the naked eye, and one of these is shown in Figure 11 with Figure 12 at 1085 x a magnified view of a part of it. The distribution and shape of the spots suggest that they were a pattern of drops of some material on the surface at a time when conditions in the converter changed. The nature of the attack seen in Figure 12 is typical of alkaline etching of Mo, and so it is suggested that droplets of Cs and possibly CsF were left on the collector surface in this pattern when it was opened to air, and the moisture in the air formed CsOH, which caused the etching attack. Therefore, this attack cannot be attributed to the Cs or CsF alone.

The metal ceramic seal of the converter was sectioned and Figures 13 and 14 are photographs of it. These show sections of the Ni flange brazed between two metallized Al_2O_3 rings with a Cu braze. Figure 13 shows the inside of the ring composite, in the Cs/CsF atmosphere, and Figure 14 shows the outside of the same section, exposed only to a vacuum. The diameter of the Ni flange in the center of the sandwich is greater than that of the Cu braze rings used, and furthermore, when the braze melts, surface tension usually tends to pull the molten metal into the space between the metallizing and the Ni, leaving a rim of bare Ni exposed. It is not, therefore, necessary to employ corrosion to explain the shape of the Ni and Cu in Figure 13; its difference from Figure 6 is due to small differences in the cross section of the parts before fabrication of the seal. A further pair of photographs, not shown, confirms the conclusion that no corrosion has occurred at the seal.

The thin-walled Ta spacer was found to be brittle. Ta is known, from wide previous experience, to be chemically inert to pure Cs, but to be embrittled by contamination with the gases C, H, O, and N. The emitter backing plate and spacer were machined as one unit from Ta bar stock. In dismantling the tube, a sharp blow caused the spacer to break away from the emitter, for almost its whole circumference, so the emitter was removed from the spacer without any cutting.

Examination of the fracture surface gave photographs like Figure 15 and 16 at 300 x: transgranular or fibrous. This is consistent with an explanation of failure depending on a widely distributed impurity, possibily a dissolved gas. A complete and final explanation is not complete at this time, but it is worth noting that the F atom has a radius comparable with C, O and N, and might have a similar embrittling effect. This possibility is under study at present, although no other workers on Ta have discussed the possibility of embrittlement by F. It is known that HF and F both attack Ta, but CsF is a stable compound, and Ta will not reduce it to Cs and TaF_2. However, TaF_2 is probably more stable than the fluorides of Re, Mo, and Cu.

CHAPTER III

PLANS FOR NEXT QUARTER

The Re-Mo system will be further investigated. Particular attention will be devoted to low CsF arrival rates. Emitter work function measurements will be conducted to the extent necessary to describe the dependence of emitter work function of the remaining variables. The W-Mo system will also be investigated The W experiments will be particularly useful in correlating this work to the work reported by other investigators who have conducted emission studies with W.

The corrosion test will continue and the duration of these tests will be lengthened.

REFERENCES

Reference 1. A. Jester and A. Minor, "Electron Emission of Tungsten in CsF Atmosphere", Conference Paper VI, ARS Conference on Ionization Phenomena in Gases, August 1963, Paris, France.

Reference 2. S. S. Kitrilakis, N. S. Rasor and L. van Someren, Semi-Annual Technical Summary Report for the Thermionic Emitter Materials Research Program, Prepared for Office of Naval Research, January, 1963.

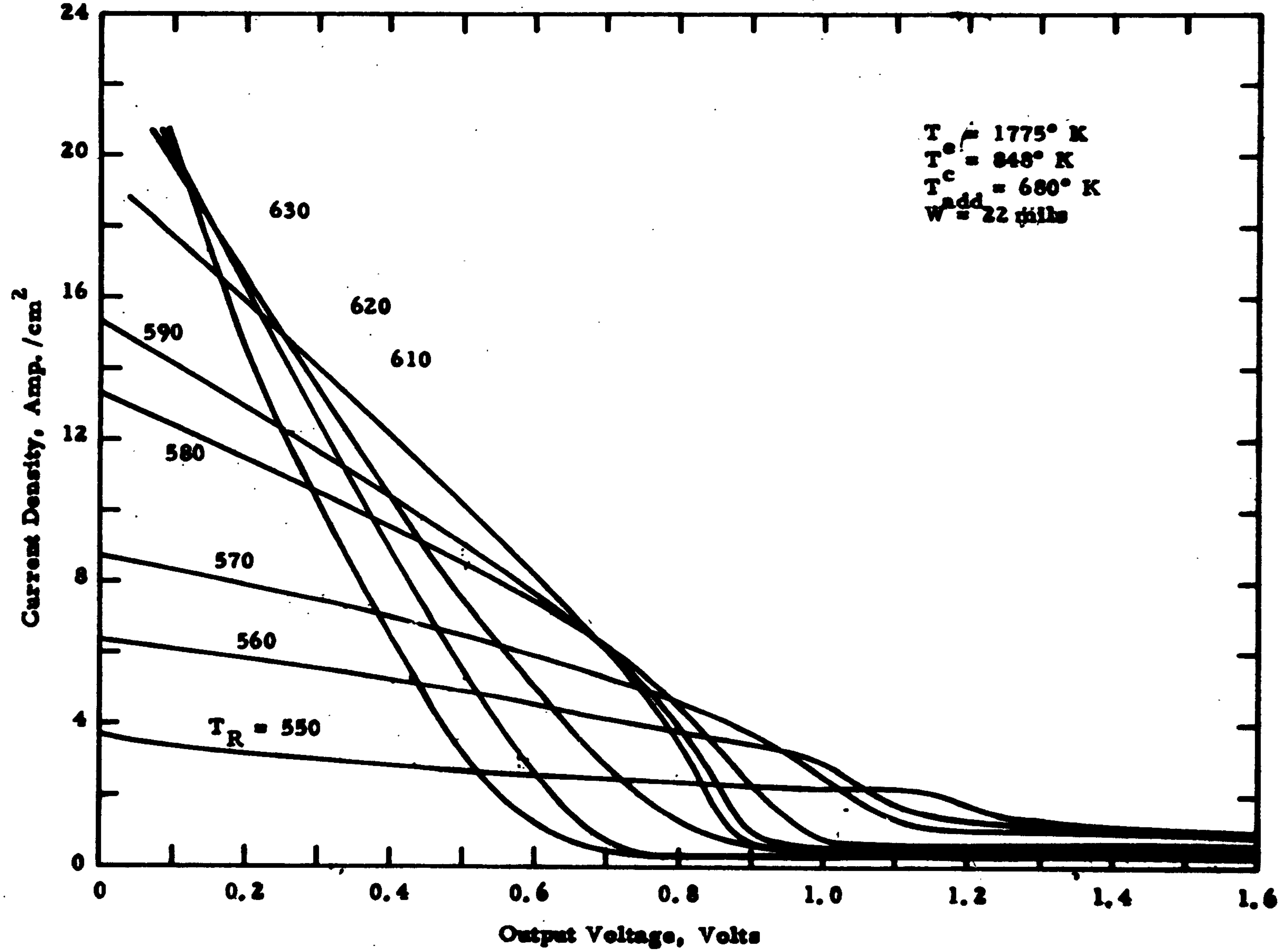

Figure 1. Family of Current-Voltage Curves
Cs and CsF present at $T_e = 1785°$ K

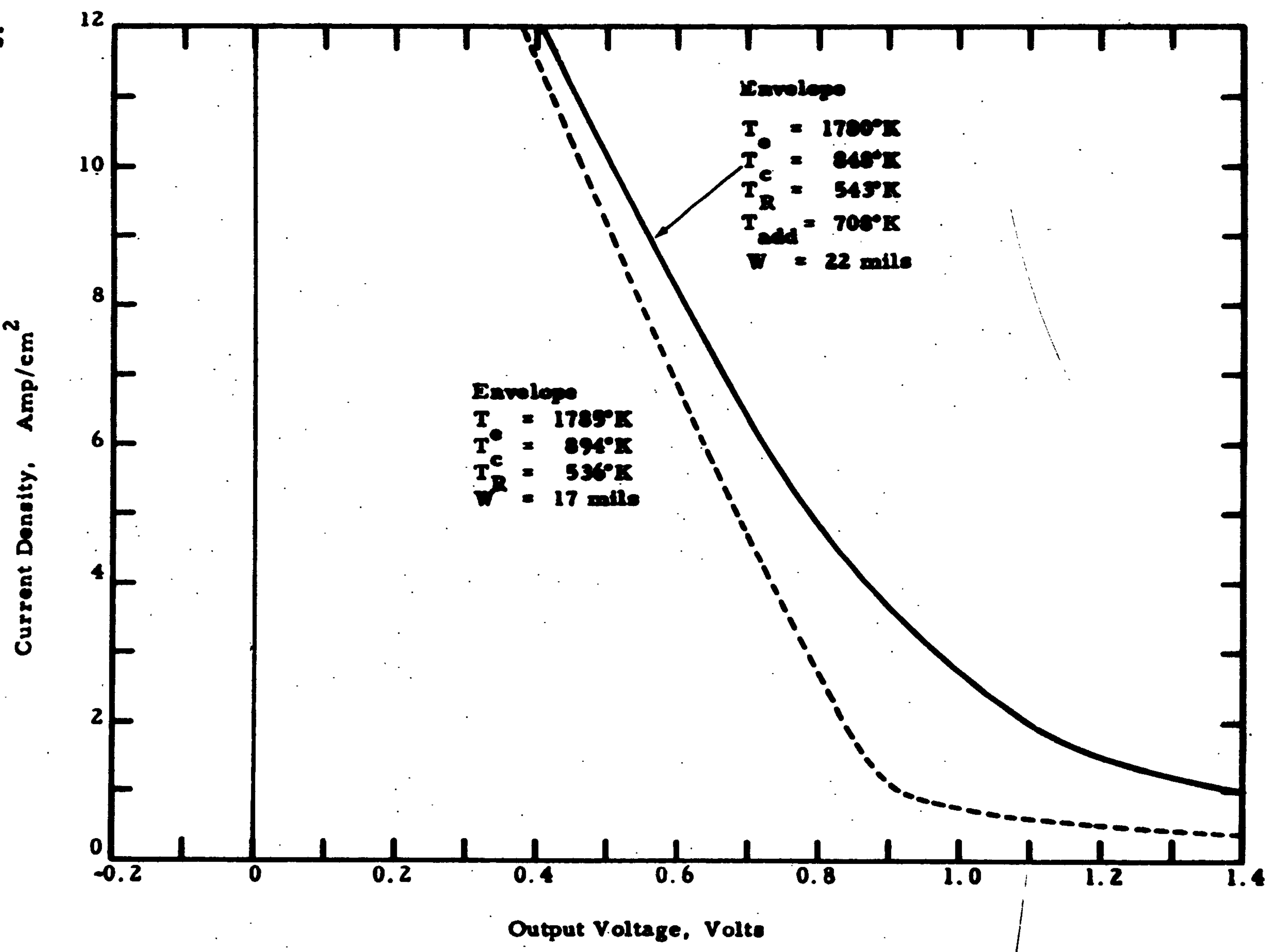

Figure 2. Comparison of Envelopes at T_e = 1785° K With and Without CsF.

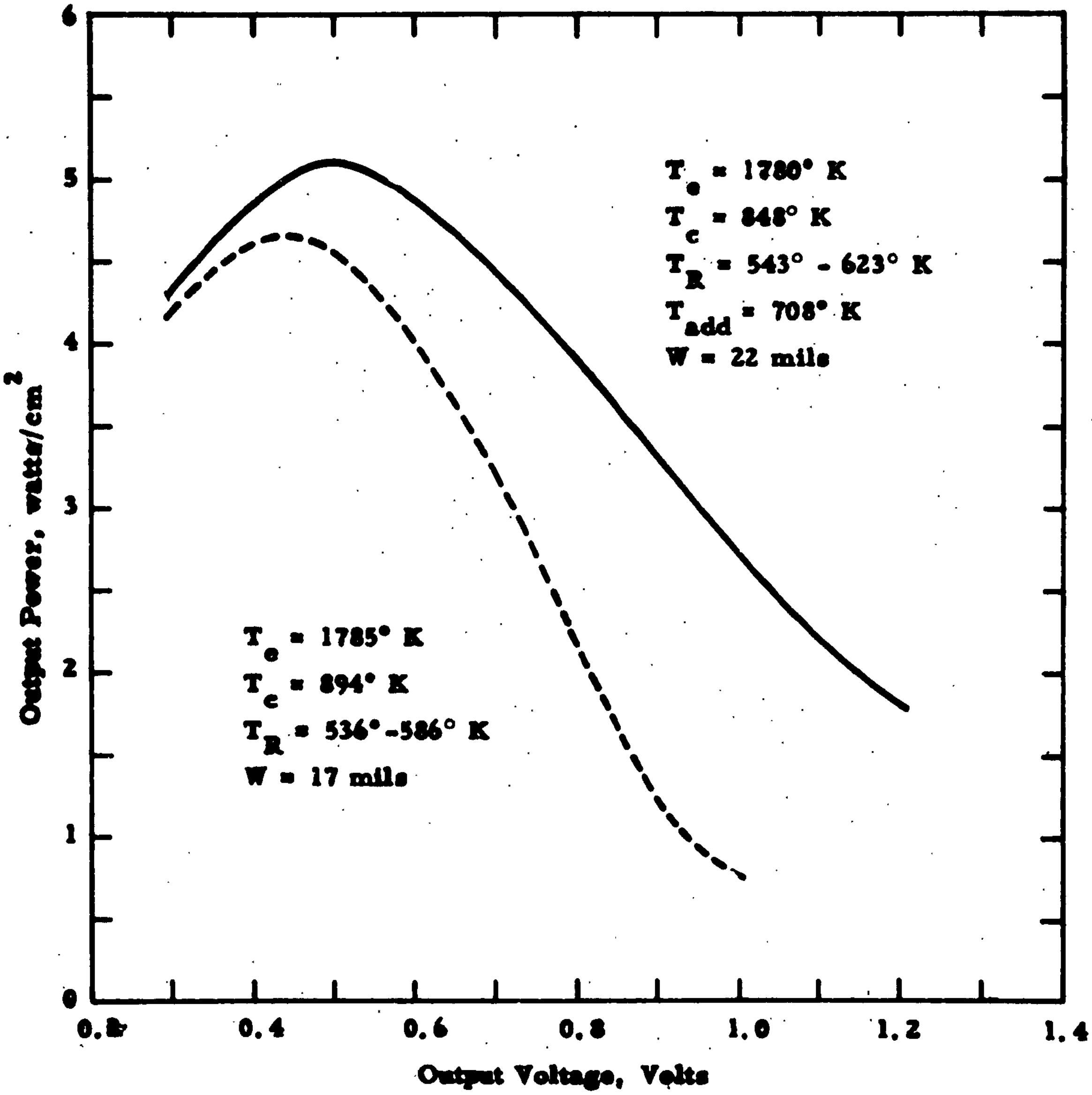

Figure 3. Power Output Comparison

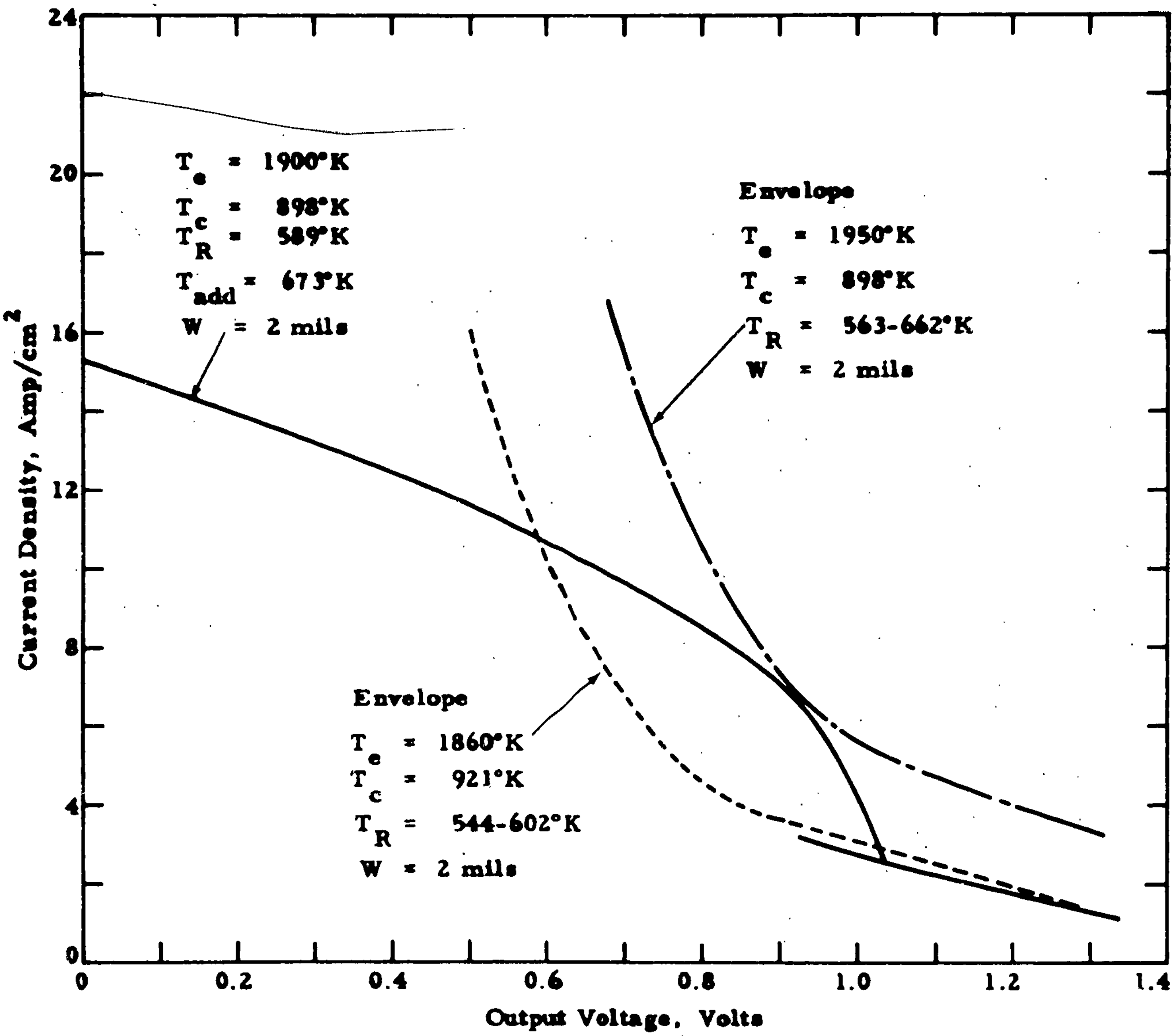

Figure 4. I-V Curves Compared to Envelopes

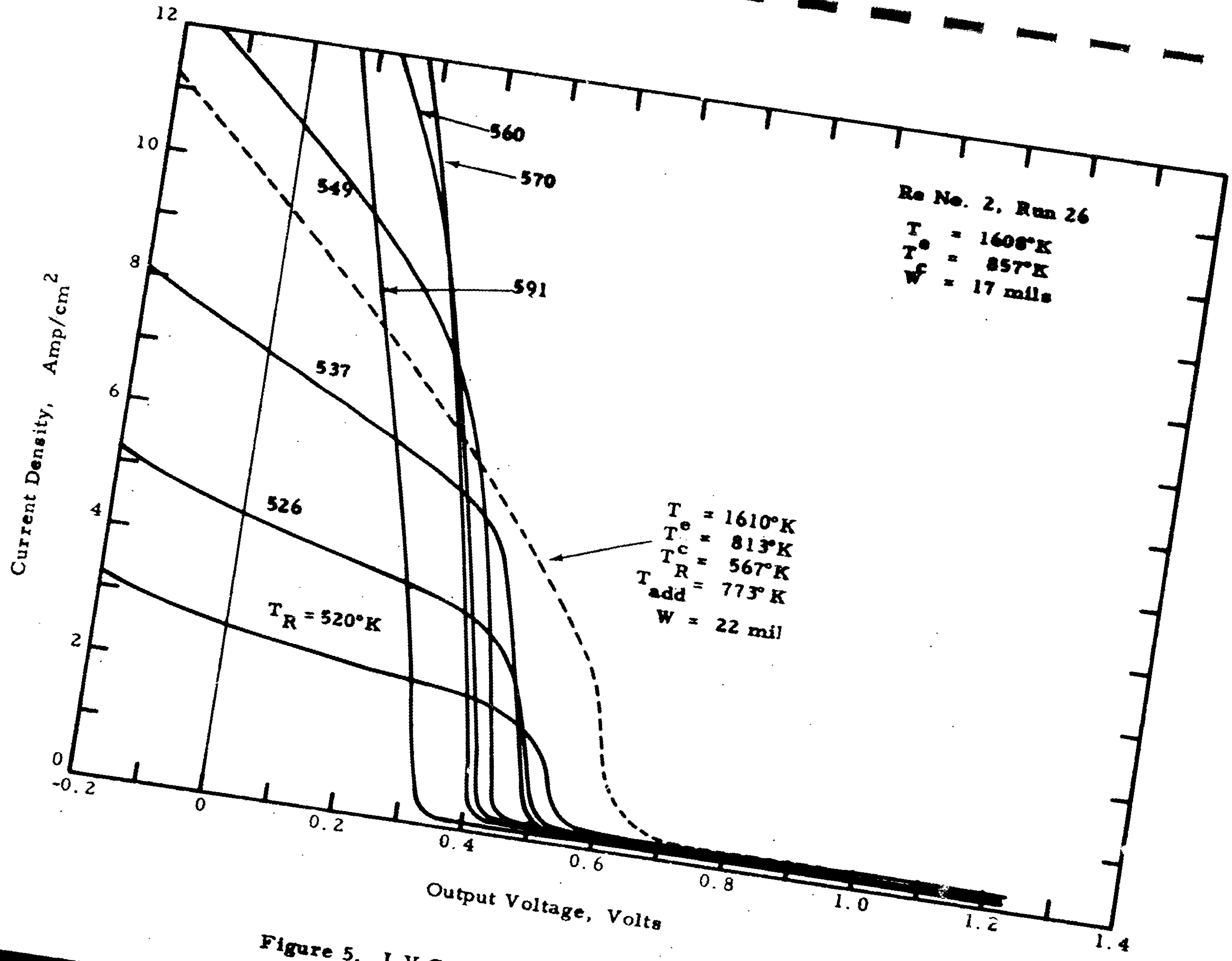

Figure 5. I-V Curves Compared to Envelopes

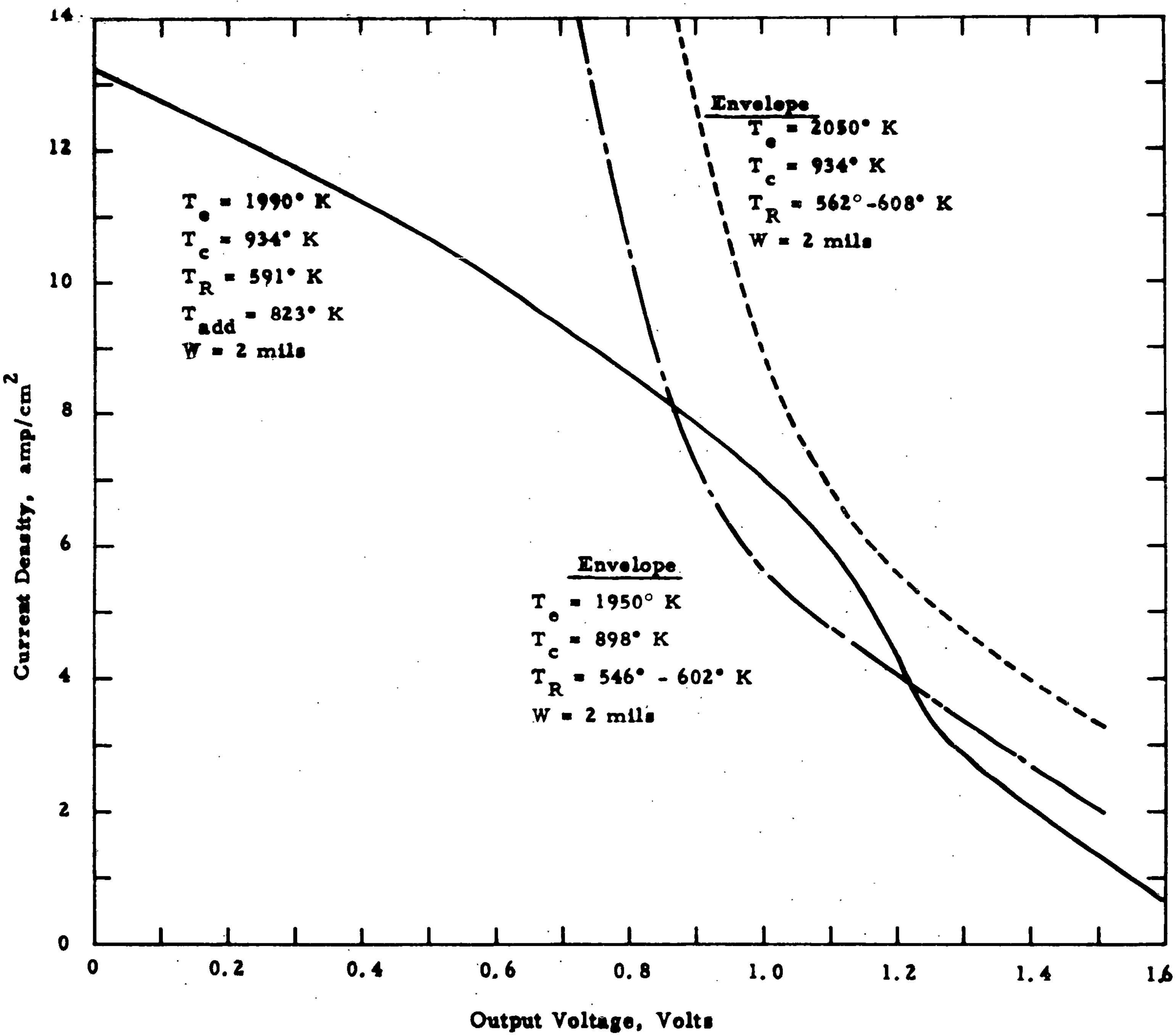

Figure 6. I-V Curves Compared to Envelopes

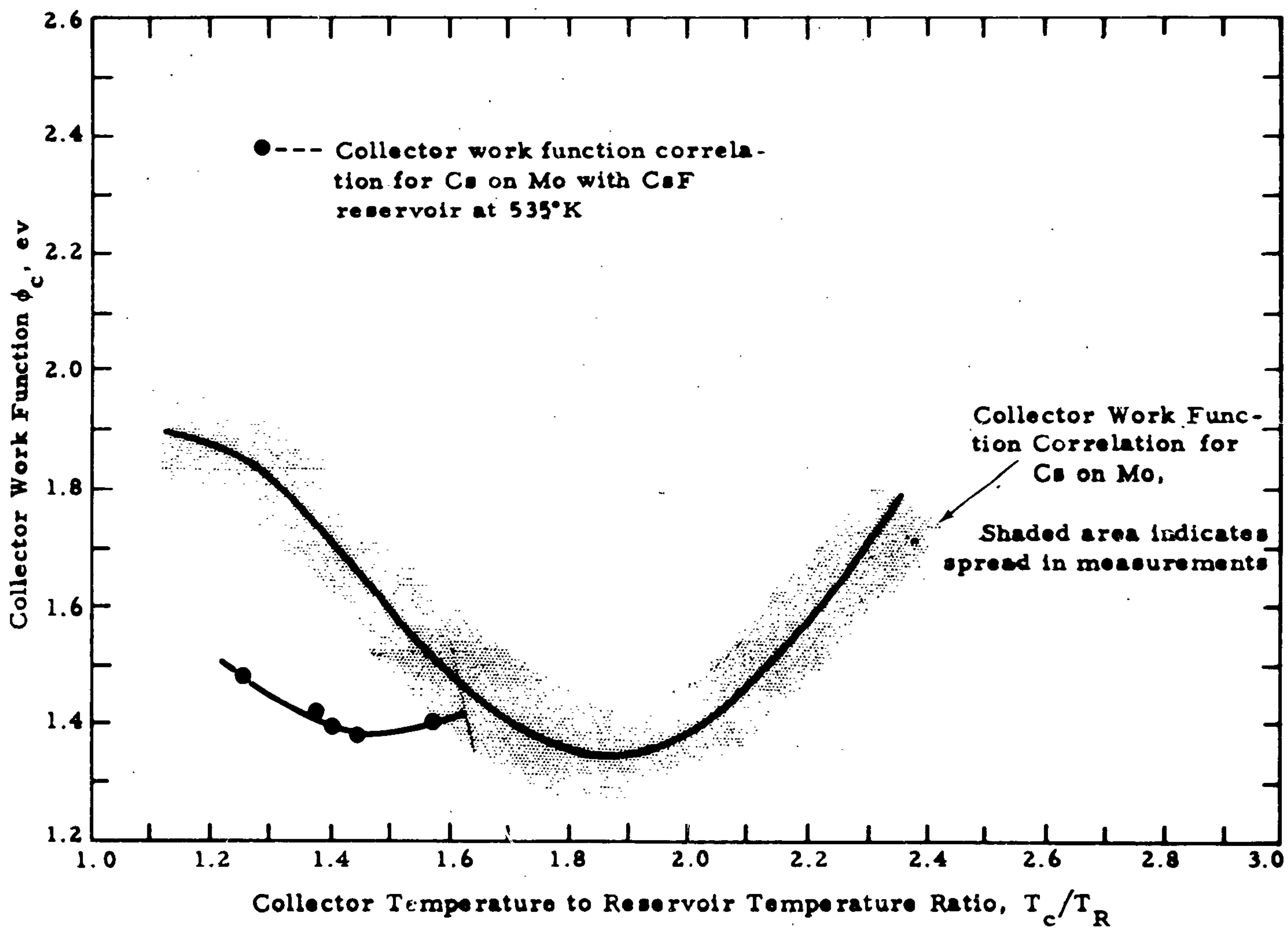

Figure 7. Collector Work Function

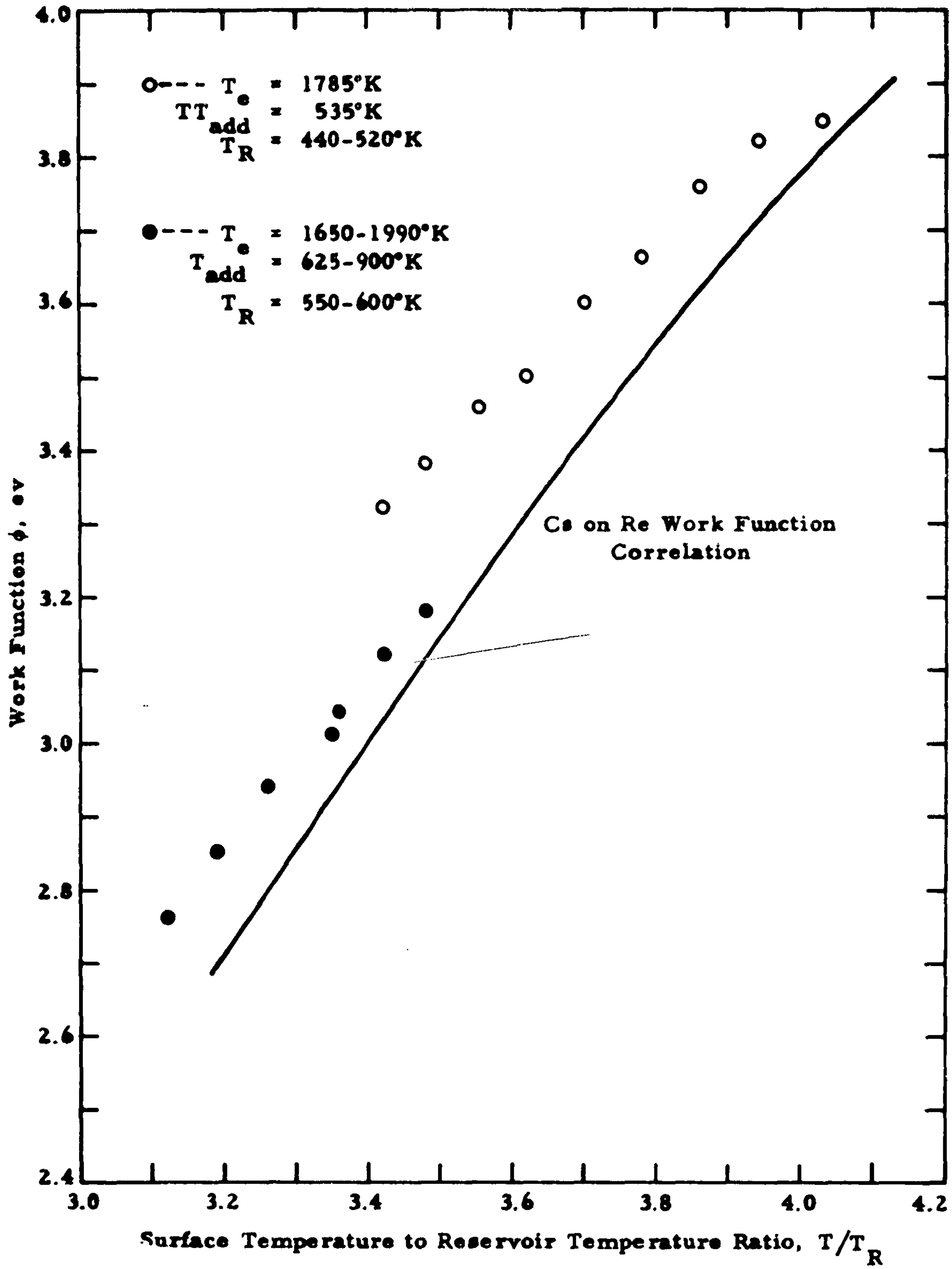

Figure 8. Emitter Work Function

Figure 9. Re Emitter Surface at 1085 x from CsF Converter

Figure 10. Re Emitter Surface from Cs Converter

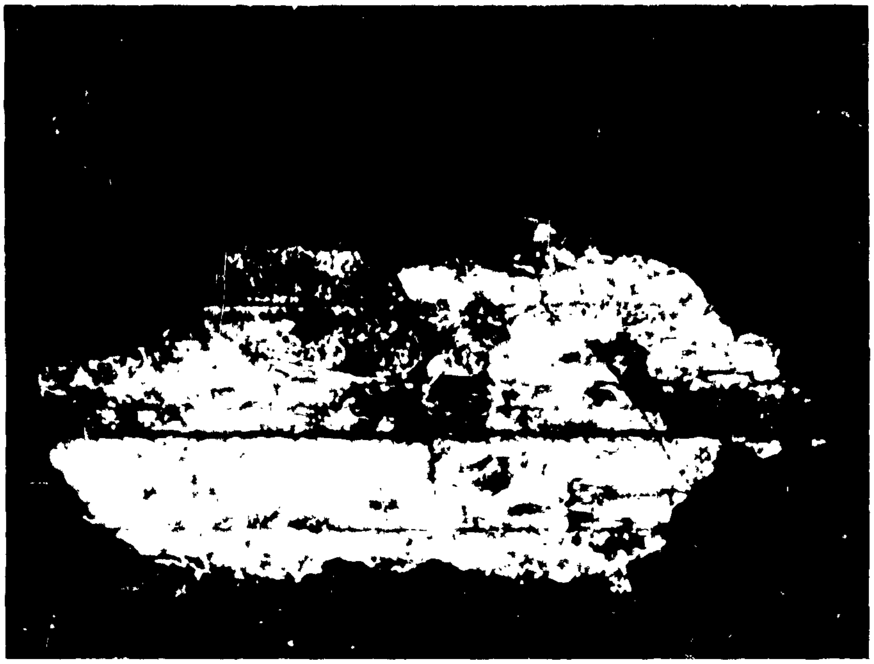

Figure 11. Mo Collector Surface at 300 x

Figure 12. Mo Collector Spot at 1085 x

Figure 13. Inside Portion of Seal at 150 x

Figure 14. Outside Portion of Seal at 150 x

Figure 15. Tantalum Thin Spacer

Figure 16. Tantalum Thin Spacer

THERMO ELECTRON
ENGINEERING CORPORATION

DISTRIBUTION LIST

CYS	ACTIVITIES AT WPAFB
1	ASAPR (Library
5	ASRPP-20
1	ASRNE-4

OTHER DEPT. OF DEFENSE ACTIVITIES

Navy

1 Office of Naval Research
Code 429
ATTN: Cmdr. John Connelly
Washington 25, D. C

Air Force

1 AFCRL (CRZAP)
L G Hanscom Field
Bedford, Massachusetts

1 SSD(SSTRE, Major W. Iller)
AF Unit Post Office
Los Angeles 45, California

11 Defense Documentation Center
Arlington Hall Station
Arlington 12, Virginia

Army

1 U S Army Signal R&D Lab.
ATTN: SIGRA/SL-PS (Dr. Kittl)
Fort Monmouth, New Jersey

OTHER U. S. GOVERNMENT AGENCIES

1 U S Atomic Energy Commission
Division of Reactor Development
ATTN: Lt. Cmdr. J. Prosser
Washington 25, D. C.

1 Advanced Research Projects Agency
ATTN: Dr. John Huth
Washington 25, D. C.

CYS	OTHER U.S GOVERNMENT AGENCIES

1 Aerospace Corporation
ATTN: Library Technical Document Group
Post Office Box 95085
Los Angeles 45, California

1 NASA - Lewis Research Center
ATTN: Library, Mr. G. Mandel
21000 Brookpark Road
Cleveland 35, Ohio

1 NASA Manned Spacecraft Center
SEDD (ATTN: J. D Murrell)
Houston, Texas

1 U.S. Atomic Energy Commission
Office of Technical Information Extension
Post Office Box 62
Oak Ridge, Tennessee

1 Institute for Defense Analysis
ATTN: Dr R Hamilton
1825 Connecticut N. W.
Washington 25, D C

OTHERS

1 Thompson Ramo Wooldridge, Inc.
New Products Research
ATTN: W. J. Leovic
23555 Euclid Avenue
Cleveland 17, Ohio

1 General Electric Company
Research Laboratory
ATTN: W. Grattidge
Post Office Box 1088
Schenectady, New York

1 Jet Propulsion Laboratory
Spacecraft Secondary Power Section
ATTN: A. Smith
4800 Oak Park Drive
Pasadena, California

1 Atomics International
ATTN: Dr. R. C. Allen
Post Office Box 309
Canoga Park, California

1 The Martin Company
ATTN: Dr. M. Talaat
Baltimore 3, Maryland

1 Radio Corporation of America
Electron Tube Division
ATTN: F. G. Block
Lancaster, Pennsylvania

1 General Motors Corporation
Allison Division
ATTN: D L Dresser
Indianapolis 6, Indiana

1 Union Carbide Corporation
Parma Research Laboratory
12900 Snow Road
Parma, Ohio

1 The Bendix Corporation
Research Laboratory Division
ATTN: George Burton
Southfield, Michigan

1 Battelle Memorial Institute
Report Library
505 King Avenue
Columbus 1, Ohio

1 Pratt & Whitney Aircraft
Division of United Aircraft
ATTN: F A Corwin
East Hartford, Connecticut